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Modulation of Pb chemical state of epitaxial lead zirconate titanate thin films under high energy irradiation

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The chemical states of epitaxial $PbZr_xTi_{1-x}O_3$ films were investigated by an X-ray photoelectron spectroscopy as a function of the gamma-ray doses. An anomalous behaviour was observed in Pb4f states, and a core level of Pb4f shifts towards a higher binding energy at 50 kGy and towards a lower binding energy at 200 kGy. The behaviour can be explained by a radiation induced reduction of PbO to metallic Pb. The metal-insulator-metal electrodes were fabricated by lithography, and the current-voltage characteristics were measured. A negative differential resistance (NDR) was observed in the leakage currents at room temperature. A higher current and disappearance of NDR characteristics were found in the 200 kGy irradiated samples, which further confirms the presence of metallic Pb. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4962860]

I. INTRODUCTION

$PbZr_xTi_{1-x}O_3$ (PZT) is one of the mostly widespread ferroelectric materials due to their applications in the radiation-hard nonvolatile random access memory, pyroelectric sensors, and field-effect transducers.[1,2] At present, the electronic properties of the electronic oxides are found crucial to functional applications, whereas a better understanding of the surface behavior would be of a significant interest. Piezoelectric/ferroelectric properties of the thin films are greatly influenced by an atomic concentration of the elements in the film and their positions in the ABO_3 internal structure.[3] The distribution of the valence electrons produces a measurable shift in the core level spectra.[2] The atomic composition with a high surface sensitivity can be measured by an X-ray photoelectron spectroscopy (XPS). The distinct advantage of the XPS is to cause a relatively less irradiation induced damage to easily reducible materials such as ions containing Pb^{2+} and considered as a non destructive technique. A significant progress has been carried out to understand the physics of a core-level photoemission from the surface of PZT; however, the surface electronic properties and even the core level spectra of such a complex oxide are still uncertain in different aspects. Fujisaki *et al.* have studied the chemical states of a degraded layer on the PZT surface and investigated the role of the surface layer in the macroscopic properties.[4] Effects of chemical etching have been studied from the XPS surface analysis, and the intensity variations of the Pb-O and Ti-O peaks were analyzed.[5] An Ar-ion etching is being used for the surface cleaning and depth profiling, and the ions had an apparent effect on the chemical compositions and lattice atom displacement in the PZT thin films.[6,7] Metallic Pb (Pb^0) and PbO (Pb^{2+}) in PZT were resolved using the Ar-ion bombardment by Chang *et al.*

and Kim *et al.* An XPS depth profiling shows the evidences of an oxygen deficiency associated with the reduction of Pb^{2+} to Pb^0 caused by the preferential sputtering of oxygen at the surface of the PZT thin films.[7,8]

It is well known that the high energy X-ray and gamma ray irradiations may result in a polarization loss and a possible retention failure in the ferroelectric thin films, as reported earlier in the $Pb(Zr,Ti)O_3$[9] and $PbTiO_3$[10] thin-film devices. Ferroelectric properties are dependent on the nature of the defects and compositions.[11] The irradiation induced performance deterioration may be more severe due to the higher possibility to be exposed to high energy irradiations for the ferroelectric thin films in the military and space applications. A high energy gamma-ray irradiation can displace a large number of atoms from their own site to the other sites, which lead to a change in the chemical environment of the atom and in turn may affect the chemical state of the atom. Recently, many of the reported studies were focused on the gamma ray irradiation on the PZT thin films, and a high radiation hardness was observed in comparison with the semiconductor materials.[12,13] Scott *et al.* reported a radiation hardness of the PZT thin film above 50 kGy of the total doses.[14] A high energy radiation induced structural changes in the device material, by changing in the atomic concentration due to the bond breaking and its possible reorganization after an irradiation.[15,16] The ferroelectric properties are important to most of the devices but have not been explored in much detail with respect to the effect of the surface chemistry in the radiation environment. Previous XPS studies for the perovskite oxides have shown different chemical states of the constituent atoms in the PZT and $BaSrTiO_3$ (BST) thin films, and surface core-level shifts have been revealed by various mechanisms including oxygen vacancies, under-coordinated atoms reduction,[17] and interface relaxation of surface.[18,19] To the best of our knowledge, there is yet no report on the effects of a gamma

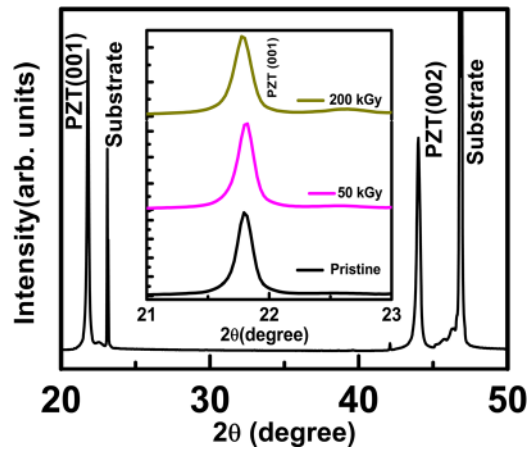[a]Author to whom correspondence should be addressed. Electronic mail: mkumar@iitj.ac.in

FIG. 1. The XRD 2θ-ω scan of the pristine PZT epitaxial film, and the inset shows the magnified (001) diffraction peak of PZT at different gamma radiation doses.

irradiation on the surface chemical states of the epitaxial PZT thin films; however, the irradiation resistance is important to the device reliability. Consequently, it is important to investigate and understand the effects of a high energy irradiation on the chemical states of epitaxial ferroelectric films for their potential use in such environment. The object of this work is to investigate the changes in the structure and chemical states of the epitaxially grown PZT thin films. In addition, we have investigated the surface roughness and leakage current characteristics of the PZT thin films as a function of gamma dose.

II. EXPERIMENTAL DETAILS

An epitaxial $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) layer (250 nm) was grown on the $SrTiO_3$ (STO) substrate using $SrRuO_3$ (SRO) bottom electrode by a pulsed laser deposition (PLD). The epitaxially perovskite oxides were grown without breaking the vacuum using a KrF excimer laser, and details on the optimized PLD growth can be found elsewhere.[20] The PZT samples were irradiated with a gamma radiation using ^{60}Co radiation source at a dose rate of 3 kGy/h up to 200 kGy. The measurements were performed before and after the gamma irradiated samples. The X-ray diffraction (XRD) 2θ-ω scans were carried out using the Cu K_α radiation to determine the

crystalline orientation and phase of the PZT film. The surface morphologies observations were investigated by using an atomic force microscope (AFM) in a tapping mode (non-contact mode). The scanning electron microscopy (SEM) characterisation was also performed on the gamma irradiated PZT films to observe the surface defects. The XPS measurements were performed using a monochromatic Al K_α radiation (1486.6 eV) with a photoemission instrumentation operating in a base pressure of 10^{-10} mbar vacuum. The XPS measurements explore the surface behaviour not more than 10 nm depth of the sample surface. The binding energies were corrected with a reference to the $C1s$ peak at 285.0 eV of the surface adventitious carbon. For the electrical characteristics measurements, circular Pt electrodes of 200 μm diameter were patterns by a photolithography technique onto the PZT films. A metal-ferroelectric-metal (MFM) structure was employed for measuring the leakage current (I-V) and capacitance-voltage (C-V) behaviours by a SCS Keithley 4020 system.

III. RESULT AND DISCUSSION

The structural characteristics of the as-grown PZT layers were evaluated by XRD and shown in Fig. 1. The PZT epitaxial layers show (001) preferred orientation except for the diffraction peaks of SRO/STO substrate. The full width half maxima (FWHM) of the (00l) peak increase with the increasing gamma doses, which can be explained by a reduced crystallinity of the film. Fig. 2 shows the AFM images of the PZT film before and after the gamma irradiation. It can be seen from the AFM images that the film tends to become rougher with an increasing gamma dose due to the radiation induced defects on the film surface and showed an increased root mean square (RMS) roughness from around 5.2 nm for pristine to 7.8 nm for 200 kGy sample. The surface morphologies of the PZT films were seen by SEM before and after irradiation, and small cracks were observed with the gamma irradiation as shown in Fig. 3. The PZT films have three components (e.g., TiO_2, PbO, and ZrO_2,) in a PZT solid solution, and the surface chemical states of the gamma irradiated PZT films were investigated with an XPS analysis. The XPS analysis for the elements of Pb, Zr, and Ti was performed to estimate the peak energies more accurately, and the peak energies were extracted by a curve-fitting on the XPS spectra. The curve fitting results were obtained by the subtraction of a
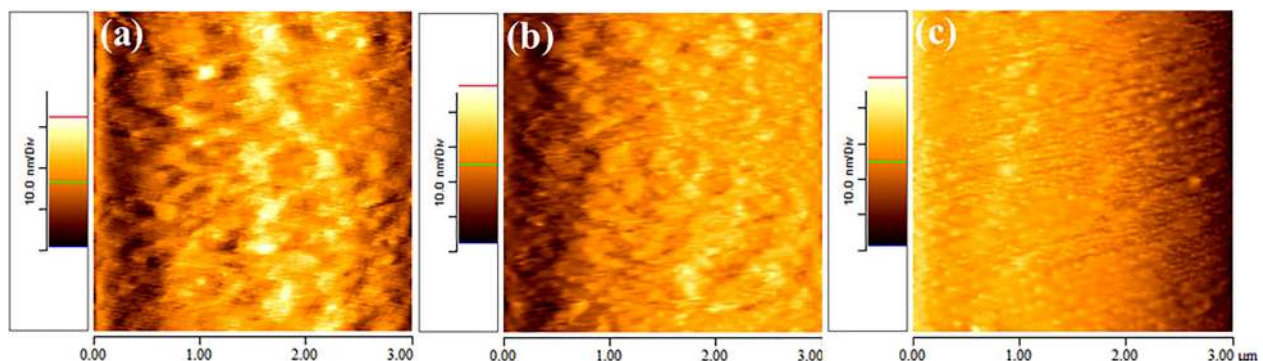

FIG. 2. The AFM images of the PZT films (a) pristine, (b) 50 KGy, and (c) 200 KGy.
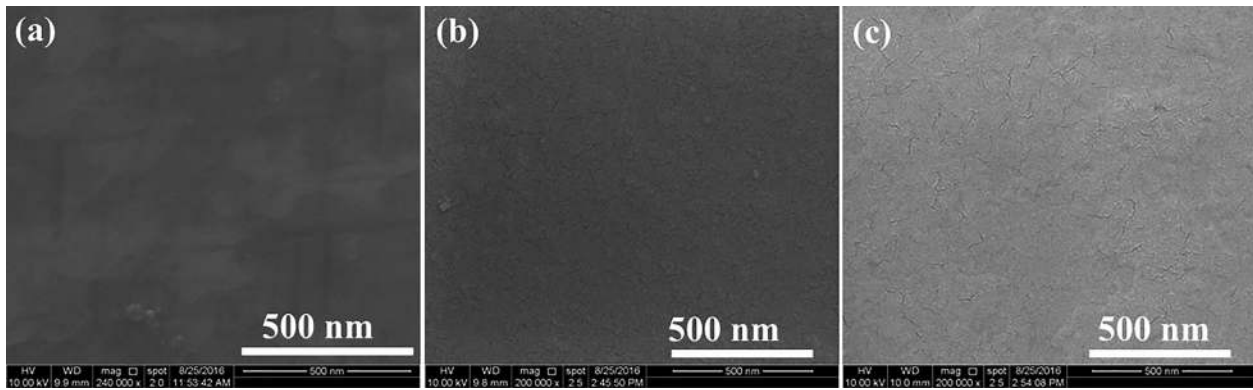
FIG. 3. The SEM images of (a) pristine, (b) 50 kGy, and (c) 200 kGy irradiated PZT films.

Shirley background, followed by a Voigt function. All the spectra of Pb, Zr, and Ti consist of two peaks corresponding to their angular moments of the electrons. The photoemission core level spectra of Pb4$f_{7/2}$ and Pb4$f_{5/2}$ spin-orbit-spin doublets are shown in Fig. 4 for the pristine and gamma irradiated samples. The Pb4f core level spectra of the pristine thin film, as shown in Fig. 4(a), are fitted with a singlet at a binding energy (BE) of 137.8 eV and 142.7 eV for 4$f_{7/2}$ and 4$f_{5/2}$ chemical states, respectively.[6] From Figs. 4(b) and 4(c), it is noted that there is a demonstration of an irregular shift with the increasing radiation doses. It was observed from this analysis that a higher binding energy shift was observed with respect to the pristine at an initial increasing dose of the gamma-ray irradiation, similar to HfO$_2$, as reported by Cheng *et al.*[21] The chemical states are shifted towards a higher BE and found at 138.1 eV (4$f_{7/2}$) and 142.9 eV (4$f_{5/2}$) at 50 kGy gamma dose as reflected from Fig. 4(b). This higher chemical

shift of lead could be attributed to the radiation induced surface relaxation or defect state of the PZT layer by the gamma radiation induced defects.[11,18,22]

The fitting for the Pb4f core level for a gamma dose of 200 kGy could not be derived by a singlet, and the curve fitting was performed with the doublets in both the 4$f_{5/2}$ and 4$f_{7/2}$ states. Moreover, the second components of Pb 4f core level spectra at a higher gamma dose of 200 kGy shifted towards a lower BE and lies at 136.8 eV (4$f_{7/2}$) and 141.9 eV (4$f_{5/2}$) because of a reduction in the metallic Pb from PbO in the PZT. At the dose of 200 kGy, the corresponding Pb 4f levels were located at about ∼1 eV lower BE than pristine, assigned as the metallic Pb peak. The emergence of the metallic Pb can be explained due to the preferential sputtering of oxygen ions and reduction of Pb^{2+} ions to metallic Pb^0.[7] As shown in Fig. 4(c), the lead atoms within the XPS investigation were found to be partially reduced to Pb^0 after a radiation exposure, as similarly reported for many oxides on Ar ion bombardment.[17,23,24] Then, the PZT surface undergoes a surface depletion of lead along with a chemical reduction of Pb^{2+} to its metallic state.[11] Possibly, the gamma radiation bombardment breaks the chemical Pb-O bond to metallic Pb and oxygen as a result of bond breaking and its reorganization in the film after gamma-irradiation.

The Zr3d and Ti2p photoemission core level spectra are shown in Figs. 5(a)–5(c) for the gamma-irradiated doses of 0 kGy (pristine), 50 kGy, and 200 kGy. The Zr3d spectra resolved into Zr3$d_{5/2}$ and Zr3$d_{3/2}$, and peaks are observed at the binding energies of 180.9 eV and 183.3 eV, respectively, for the pristine film. From the Ti2p XPS spectra of pristine, the Ti2$p_{3/2}$ and Ti2$p_{1/2}$ peaks are observed at the binding energies of 457.5 eV and 462.8 eV, respectively. The Zr3d and Ti2p line shapes at all the doses can be described by a chemical shift towards a higher BE. The higher binding energy shifts were attributed to Zr and Ti atoms in a relaxed surface[11,18,22] similar to the Pb atoms. The Zr3d and Ti2p spectra do not exhibit any noticeable change towards a lower binding energy.

Fig. 6 displays the dependence of the leakage current of the capacitor as a function of applied bias at a different gamma dose up to 200 kGy. The dip in the current of pristine device has been described as a negative differential resistance
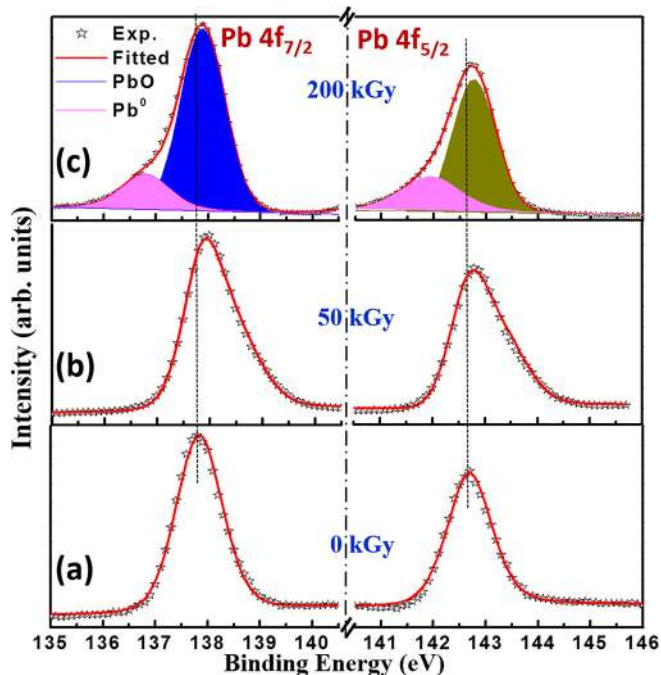

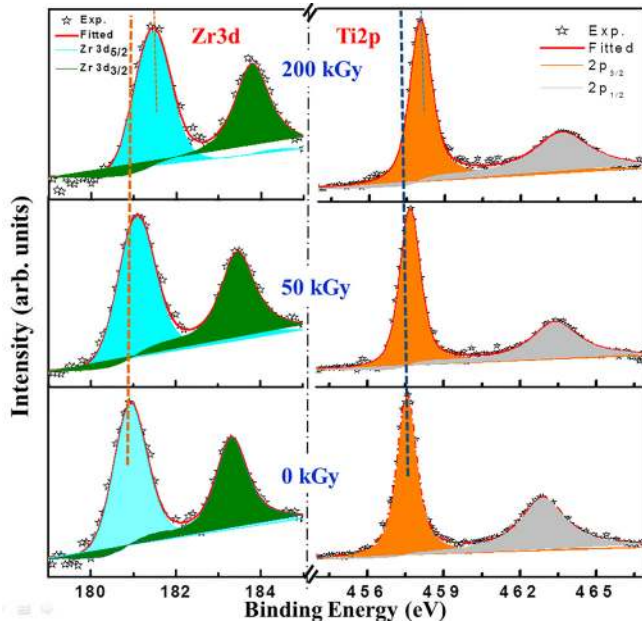FIG. 4. The XPS core level spectra of Pb 4f (4$f_{7/2}$ and 4$f_{5/2}$) at (a) pristine, (b) 50 kGy, and (c) 200 kGy.

FIG. 5. The XPS core level spectra of Zr 3 d *(3d$_{5/2}$ and 3d$_{3/2}$)* and Ti 2 p *(2p$_{3/2}$ and 2p$_{1/2}$)* at (a) pristine, (b) 50 kGy, and (c) 200 kGy.

FIG. 6. The leakage current characteristics of a Pt/PZT capacitor as a function of the gamma dose.

(NDR) by Scott *et al.*,[25] caused as a result of a double injection of both the electrons and the holes into PZT from the electrode and trap filling process.[26,27] The increase in the leakage current after the gamma irradiation along with a barrier reduction may be expected to be caused by the migration of oxygen from the surface as well as loss from the bulk.[17] Dih and Fulrath[28] have reported the role of oxygen in increasing the conductivity. The increasing leakage current may be attributed to the gamma radiation induced defects in the PZT film. The reduced Pb^{2+} in PZT contains some missing oxygen ions, where each missing O^{2-} ion requires two additional electrons to maintain the electrical neutrality.[17] The valency of the metal ion should reduce in such reduced metal oxides so that the free electrons might be available for contribution in the increasing current.[29] The increase in the leakage current and the disappearance of NDR were associated with a metallic Pb produced by the gamma irradiation. Fig. 7 shows *C-V* hysteresis at 100 kHz for the pristine and gamma irradiated samples. The *C-V* hysteresis curves reveal a decrease in the charge accumulation with the increases in gamma doses, indicating a significant loss in a macroscopic polarization,
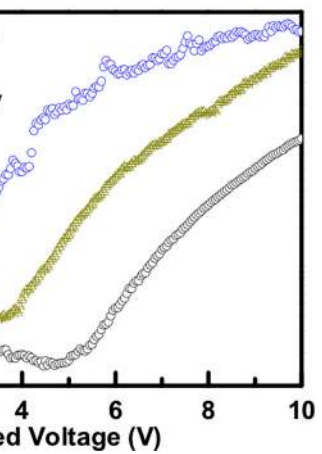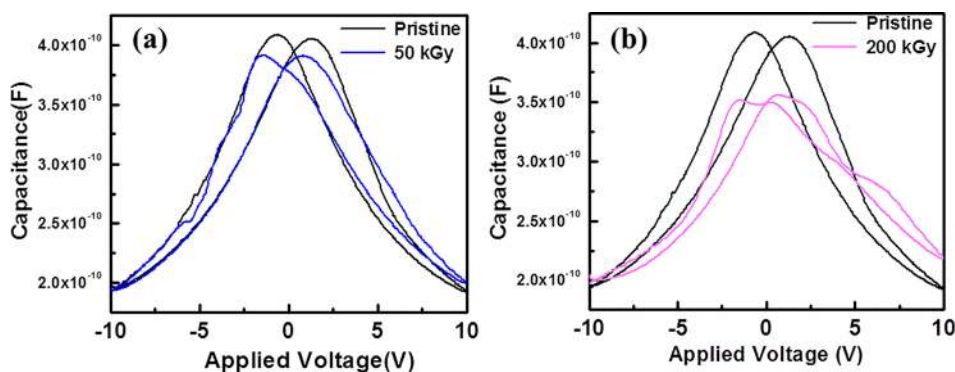
which is closely related with the piezoelectric properties as well.

The PZT films may be protected from a high energy radiation by employing the following approaches (independently or in combination): (i) physical shielding, (ii) electronics hardened, and (iii) oxide and nitride passivation layer to improve the radiation sustainability of the devices.[30,31]

IV. CONCLUSION

The dependence of the chemical states of the constituent elements of the PZT thin film on the gamma irradiation doses were investigated using the XPS. The different binding energies of the Pb lines corresponding to both Pb (2+) and metallic Pb (0) were observed. The high BE shift of the Pb lines for an initial gamma dose followed by shifting towards a lower BE at the surface layer were attributable to the surface relaxation and reduction mechanism of Pb, respectively. The Ti2*p* and Zr4*f* lines in the PZT film could have been associated with surface relaxation only and reflected towards a higher BE shift with an increasing irradiation dose. This study has shown the effects of the gamma radiation induced defects on the structure and dielectric properties. As expected, an increase in the surface roughness with the increasing gamma dose in turn decreases the crystallinity. The NDR behaviour in the pristine PZT was found to disappear at a gamma dose of 200 kGy and in turn favours the

FIG. 7. The C-V hysteresis measurement as a function of applied bias at 100 kHz for the gamma irradiated PZT varactor at (a) 50 kGy and (b) 200 kGy.

presence of a metallic Pb in the PZT film. These results corroborate the increase of the leakage current of a Pt/PZT capacitor as a function of gamma dose.

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